COMBUSTION IN COPPER (I) OXIDE WASTE-NiO-NH$_4$NO$_3$ SYSTEM AND SYNTHESIS OF Cu-Ni ALLOYS

H. A. MAHMOUDI[*1,3], V. V. VARDAPETYAN[1], L. S. ABOVYAN[2] and S. L. KHARATYAN[1,2]

[1]Yerevan State University
1, A. Manoukyan Str., Yerevan, 0025, Armenia
[2]A.B. Nalbandyan Institute of Chemical Physics NAS RA
5/2, P. Sevak Str., Yerevan, 0014, Armenia
[3]National Iranian Copper Industries Company (NICICO), Kerman, Iran
E-mail: mahmoody.h@gmail.com
E-mail: larisa@ichph.sci.am

In this work the reactions thermal coupling approach was applied for the joint reduction of Cu and Ni from the mixture of copper (I) oxide waste and nickel (II) oxide in the combustion mode, targeting the preparation of Cu+Ni composite powders and Cu-Ni alloys in a single step. The experiments for reduction of both the metals in the combustion wave were implemented in the presence of ammonium nitrate (Nt) without introducing any additional reducing agent. To achieve complete reduction of metals, combustion laws in the Cu$_2$O(oily waste)-NiO-Nt system by using copper oxide (I) waste with different content of oil and at different ratios of metal oxides in the initial mixture were investigated. Optimal conditions for obtaining Cu+Ni composite powders and Cu-Ni alloys from copper waste and NiO powder depending on the content of oil and ammonium nitrate were determined.

Figs. 8, references 19.

Introduction

Alloys based on copper and nickel are distinguished by excellent mechanical properties, corrosion resistance, technological effectiveness and special electrical properties, which lead to their widespread use in different technologies. Copper-nickel alloys are used in the electrical engineering, shipbuilding, aviation and space industry, in the production of nuclear reactors, medical equipment, dishes, devices with shape memory, for special coatings, as well as catalysts for the hydrogenation of various organic compounds, for deep

oxidation of CO and various hydrocarbons, dry reforming of methane with carbon dioxide, etc. [1,2].

In the wiring industry at production of copper wires and cables about 0.6-0.7 wt.% of copper is converted into waste representing mainly copper (I) oxide [3]. Therewith, on all stages of rolling for decreasing the friction forces of moving details, as well as preventing deep oxidation of the metal, hydrocarbon-based mineral oils are used as lubricants. Utilization of such wastes requires reliable methods for their reprocessing back into copper [4-5].

One of the ways for utilization of the oily copper wastes is to remove the oil with a suitable organic solvent and then reduce the oil-free waste to metallic copper. For this purpose, one can use both traditional furnace methods using carbon or hydrogen as a reducing agent [1,6,7] and the method of self-propagating high-temperature synthesis (SHS) [8,9] using a combined reducing agent: polystyrene [10-12].

The possibility of copper (II) oxide reduction under the combustion mode has been shown for the first time in [10] by using combined organic reducers: polystyrene (PS), polyethylene (PE), urotropin, etc. Then this approach was developed in [11-15] and extended for reduction of other oxides (Cu_2O, NiO, CoO, Co_3O_4) and oxygenous salts ($Ni_2(OH)_2CO_3$, $Cu_2(OH)_2CO_3$, $CoSO_4$), as well as for joint reduction of CuO with Cu_2O, CuO with NiO, NiO with Co_3O_4 to produce metal powders and alloys. In these cases, for which the reduction by polystyrene are weak exothermic reactions, it becomes necessary to use a high-caloric additive, containing polystyrene and a strong oxidizer – NH_4NO_3 (hereinafter Nt) and apply the coupling of low-caloric MeO+PS and high-caloric PS+Nt reactions approach in the combustion mode [16,17].

In the work [18] copper (I) oxide waste reduction was studied after preliminary removing the oil, which is a labor-intensive and expensive procedure. It was shown that complete reduction of copper from copper (I) oxide waste in the combustion mode is possible by using the PS+Nt mixture. Recently the complete reduction of copper from oily copper waste in the combustion mode was performed without preliminary cleaning stage adding only ammonium nitrate to the initial mixture. It was supposed that due to its hydrocarbonic nature, the oil could serve as a combined reducer instead of polystyrene for reduction of copper (I) oxide [19].

In this work the reactions' thermal coupling approach was applied for the joint reduction of copper (I) oxide waste and nickel oxide in the combustion mode targeting the preparation of composite powders and Cu-Ni alloys in a single step. To achieve this aim, combustion laws in the Cu_2O(oily waste)-NiO-Nt system by using the copper oxide (I) waste with different content of oil and at different ratios of metal oxides in the initial mixture were investigated. In this case, as well as at reduction of oily copper (I) oxide waste [19] the proposed approach intends to take the advantage of the hydrocarbonic nature of the oil and utilize it as a combined reducer for the joint reduction of copper and nickel

410

oxides. For increasing the exothermic effect of low caloric $Cu_2O+C_nH_m$ and $NiO+C_nH_m$ reactions and performing joint reduction of both the oxides to metallic Cu and Ni in combustion mode, the reactions' thermal coupling approach was applied.

Determination of optimal conditions of the process was based on the results of preliminary thermodynamic calculations for the system under study. Note that at certain ratio of the reagents the adiabatic temperature for PS + Nt reaction reaches 2000^oC. Close values of T_{ad} were attained at using other hydrocarbons instead of PS, including the above mentioned mineral oils. In the case of Cu_2O–NiO-C_nH_m-Nt system the adiabatic temperature for the combined combustion-reduction process is within the range of 700-1200^oC, which is sufficient for self-sustained reduction of copper and nickel oxides.

Materials and methods

The copper-containing oily waste of wiring industry used in this work represents mainly copper (I) oxide with small amount of metallic copper and comprises plate-like particles with linear size up to 1.6 *mm* (particles with linear size less than 0.4 *mm* account for about 90 wt.%) and thickness up to 0.25 *mm*. The composition of the initial copper waste was examined by XRD analysis (Fig. 1a) and particle size distribution was determined by sieve analysis (Fig. 1b). The content of mineral oil (a mixture of various unsaturated and saturated aliphatic and aromatic hydrocarbons, hereinafter C_nH_m) in the copper waste determined by the mass loss after diethyl ether treatment typically was up to 5 wt.%, and for special cases reached up to 15 wt.%. The content of carbon and hydrogen in the oil were approximately 85 and 15 wt.%, respectively.
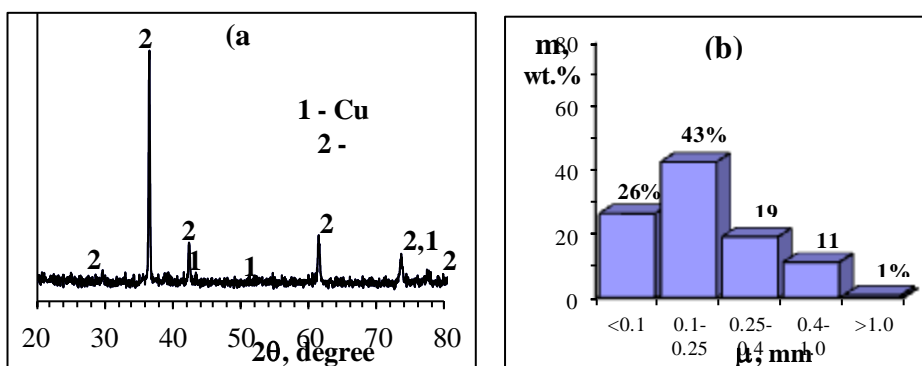

Fig. 1. XRD pattern (a) and histogram (b) of the inital copper (I) oxide waste.

Copper waste with particle size less than 1.6 *mm*, containing different amounts of oil (11 and 15 wt.%), nickel oxide powder (Pure grade, Russia) with particle size less than 0.1 *mm* (<0.05 *mm* - ~95 wt.%) and granulated ammonium

nitrate with granule size less than 3 *mm* (mark B, high grade, GOST 2-85, Russia) were used as the initial reagents (Fig. 2).

In experiments cylindrical pellets 20 *mm* in diameter and 45-50 *mm* height with $2.0 \div 2.5$ $g \cdot cm^{-3}$ density (relative density: $\Delta = 0.3 \div 0.5$) were prepared from initial mixtures: $[Cu_2O + \mathbf{m}(oil)] + \mathbf{y}NiO + \mathbf{x}(Nt)$. Main variables in combustion experiments were $\mathbf{x}$ *(moles)*, $\mathbf{y}$ *(moles)* and $\mathbf{m}$ (wt.%) values. The prepared samples were placed in a reaction chamber CPR-2.5 L. The reactor was sealed, evacuated, purged with nitrogen (purity 99.97 %, oxygen content less than 0.02%) and filled to the desired pressure (typically 0.5 *MPa*). The combustion process was initiated with short heating of tungsten spiral (18 *V*, 2 *s*) from the upper surface of the sample. Combustion temperature (T_c) and combustion velocity (U_c) were measured by two K-type chromel-alumel thermocouples (with 0.2 *mm* in diameter) covered with a thin layer of boron nitride. The thermocouples were placed into the sample with depth of 10 *mm*, and 15-20 *mm* distance from each other. The standard errors of measurement for T_c and U_c were $\pm 10^{\circ}C$ and 5%, respectively. The output signals of thermocouples were transformed by a multichannel acquisition system and recorded by a computer with frequency up to 1 KHz. After cooling, the reacted samples were extracted from the reactor and crushed into a powder. Final products were examined by XRD analysis with monochromatic CuK_α radiation, wavelength 1.54056 Å (diffractometer DRON-3.0, Burevestnik, Russia) operated at 25 kV and 10 *mA*. To identify the products from the XRD spectra, the data were processed using the JCPDS database. The microstructure of powders was examined by scanning electron microscopes BS-300 and CamScan MV2300. Carbon content in the final product and in oil was determined using Leco SC-444 carbon/sulfur analyzer.

Results and discussion

Combustion laws of the Cu_2O(oily waste) + $yNiO$ + xNH_4NO_3 mixtures

Combustion experiments for the $[Cu_2O + \mathbf{m}$ (oil)$] + \mathbf{y}NiO + \mathbf{x}(Nt)$ mixtures were carried out in a wide range of the parameter $\mathbf{x}$ ($0 \leq \mathbf{x} \leq 1.2$) for copper waste with different contents of oil ($\mathbf{m}$) and different ratios of metal oxides ($\mathbf{y}$) in the initial mixture. The dependences of the combustion temperature and velocity, as well as mass loss of the samples versus parameters $\mathbf{x}, \mathbf{m}$ and $\mathbf{y}$ were obtained, the chemical and phase compositions of the combustion products were determined. The reduction degree of the metals from oxides was primarily estimated from mass loss of the samples after combustion.

The choice of specific values and ranges of the parameters *m* and *y* was carried out on the basis of the data of combustion diagram for the $[Cu_2O$ - $\mathbf{m}(oil)] - \mathbf{x}(Nt)$ system in the coordinates *m*(oil) - *x* (Nt) [10]. For experimental studies, two batches of waste with an oil content of *m* = 11, 15 wt.% and two compositions with a nickel oxide content of: *y* = 1 and 2 mol were selected. For
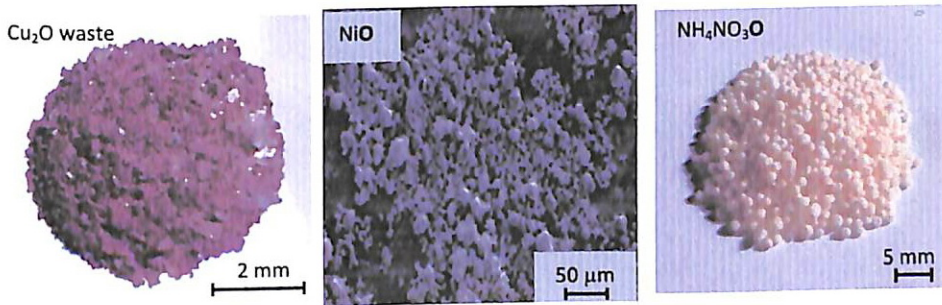
Fig. 2. Photos/micrograph of the inital copper (I) oxide oily waste, nickel oxide and ammonium nitrate.

each case the effect of the content of ammonium nitrate on the combustion laws, phase and chemical composition of the combustion products was studied.

Combustion laws of the [Cu₂O+11 wt.% (oil)] + yNiO + x(Nt) mixtures

The experimental results obtained for the [Cu$_2$O+11% (oil)]+NiO+x(Nt) and [Cu$_2$O+11%(oil)]+2NiO+x(Nt) mixtures at varying the parameter x in the intervals 0<x≤0.9 and 0<x≤1.2, respectively, are presented in Figures 3 and 4. As can be seen from Fig. 3a, at x = 0.2, a lower combustion limit is observed for the ammonium nitrate content in the initial mixture y=1. In the case of y=2 (Fig. 3b) a noticeable shift in the lower combustion limit (x=0.25) is observed towards high values of the parameter x. Figure 3 also shows that in both cases, an increase in the parameter x leads to an increase in both the combustion temperature and velocity, as well as the loss in sample mass (Δm), which is associated with increasing the share of the strong exothermic reaction (C$_n$H$_m$+Nt) in the total process.

It should be noted that in the studied intervals of the parameter x, namely at 0.25≤x≤0.9 and 0.35≤x≤1.2 increase in the combustion parameters (T$_c$ and U$_c$) shows a tendency to saturation. Figure 3a, b compares also the calculated mass loss data for complete joint reduction of metals (Cu, Ni) from a mixture of the corresponding oxides (solid curve) with experimental values (points) for different x values. The mismatch between the calculated and experimental values in the mass loss indicates to incompleteness of metal reduction and the presence of unreacted oxides of one or both metals in the final products.
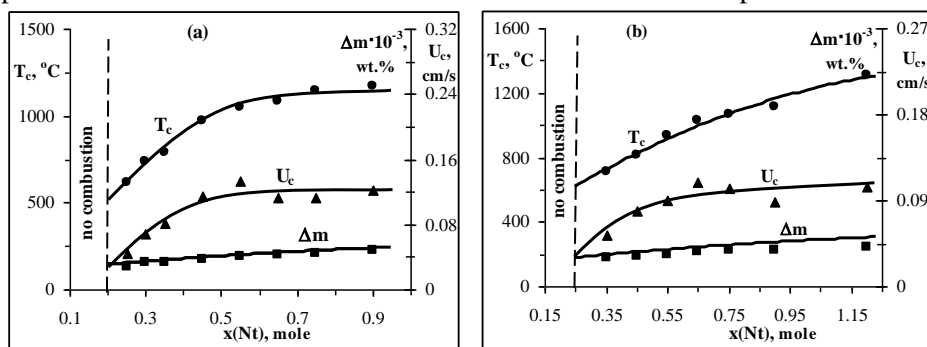

Fig. 3. Combustion temperature (T$_c$), velocity (U$_c$) and mass loss (Δm) vs. x value for the [Cu$_2$O-11wt.%(oil)]-NiO-x(Nt) (a) and [Cu$_2$O-11wt.%(oil)]-2NiO-x(Nt) (b) systems.

According to the results of XRD analysis, for both the systems under consideration, in the whole range of x parameter variation, complete reduction of the metals does not take place. Combustion products, except the reduced metals, contain also the oxides of corresponding metals, mainly NiO (Fig. 4). Note, that formation of monophase Cu-0.5Ni alloy (containing 32 wt.% Ni) and Cu-Ni alloy (containing 48 wt.% Ni) even at relatively high combustion temperatures has not been observed for lack of sufficient amount of the reducing agent (oil). Carbon content in the combustion products was measured to be 0.07-0.20 wt.%, at that low content of carbon was observed at higher amount of Nt.
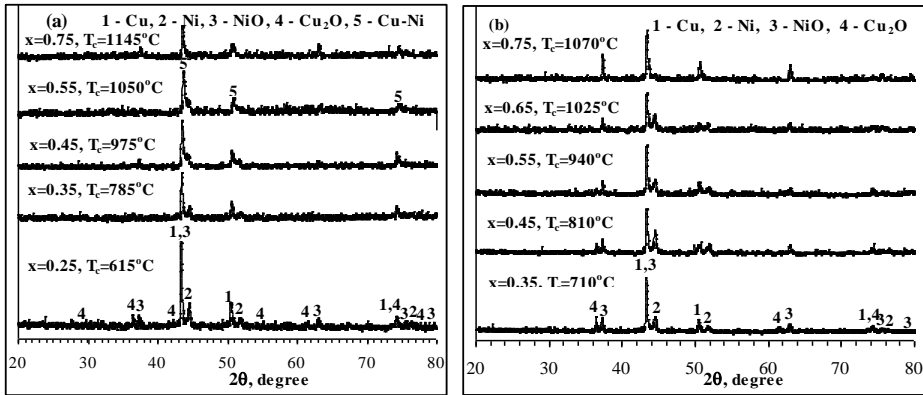
413

Fig. 4. XRD patterns of the combustion products for the [Cu_2O-11 wt.%(oil)]-NiO-**x**(Nt) (a) and [Cu_2O-11wt.%(oil)]-2NiO-**x**(Nt) (b) systems at different **x** values.

Thus, full joint reduction of both the metals and formation of Cu-Ni composite powders and alloys under the combustion mode by using copper waste with 11 wt.% of the oil content was not observed. Copper waste containing 11 wt.% of oil can be used only for obtaining Cu-Ni alloys with less than 32 wt.% of Ni. So for the SHS processing of the copper waste to Cu-0.5Ni and Cu-Ni alloys it is necessary to use copper waste with higher (more than 11 wt.%) content of oil.

Combustion laws of the [Cu_2O+15 wt.% (oil)]+yNiO+x(Nt) mixtures

In Figures 5 and 6 the results for combustion of the [Cu_2O-15wt.%(oil)]-**y**NiO-**x**(Nt) system at **y**=1 and 2 are presented. In this case lower combustion limit is observed at the same values (**x**=0.2 and **x**=0.25) as for the copper waste with 11 wt.% content of oil. It is obvious that increase in the parameter **x** in the intervals of 0.2<**x**≤0.9 (Fig. 5a) and 0.25<**x**≤1.2 (Fig. 5b) leads to the increase in both the combustion temperature and velocity, as well as in the mass loss of the samples (**Δm**), which is associated with an increase in the portion of the strong exothermic reaction (C_nH_m + Nt) in the total process similar to the case of using copper waste with 11 wt.% content of oil. Thus, combustion in the mentioned system leads to complete reduction of both the metals and formation of solid solutions or alloys of the reduced metals.
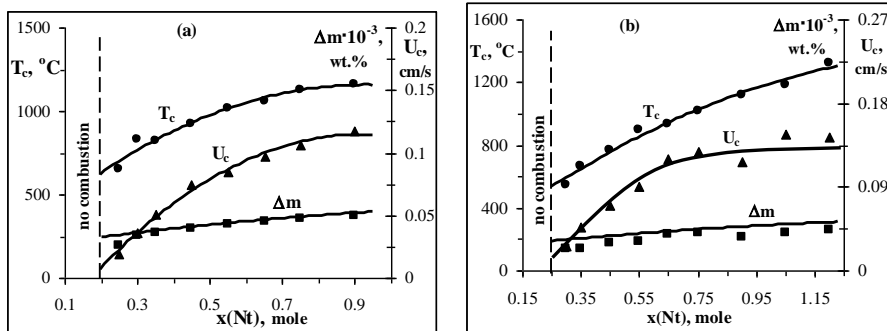

Fig. 5. Combustion temperature (T_c), velocity (U_c) and mass loss (Δm) vs. **x** for the [Cu_2O-15wt.%(oil)]-NiO-**x**(Nt) (a) and [Cu_2O-15wt.%(oil)]-2NiO-**x**(Nt) (b) systems.

414
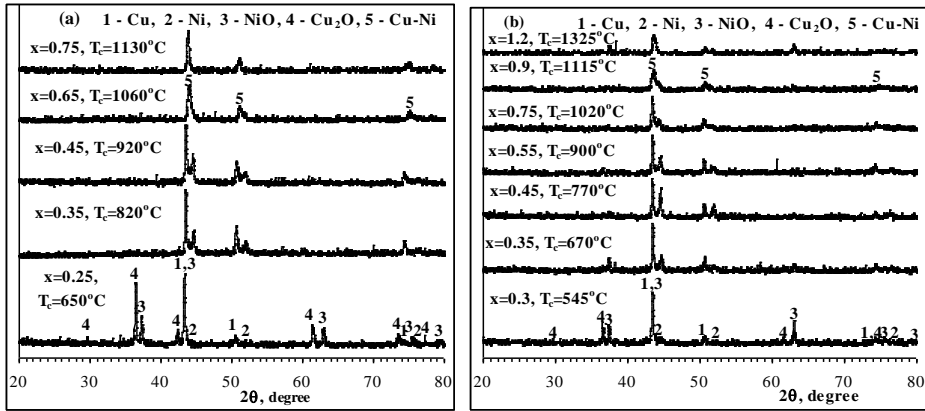
Fig. 6. XRD patterns of the combustion products for the $[Cu_2O-15wt.\%(oil)]-NiO-\mathbf{x}(Nt)$ (a) and $[Cu_2O-15wt.\%(oil)]-2NiO-\mathbf{x}(Nt)$ (b) systems at different **x** values.

According to the results of XRD analysis, in the case of the $[Cu_2O-15wt.\%(oil)]-NiO-\mathbf{x}(Nt)$ system complete reduction of both the metals takes place with formation of a monophase product at $\mathbf{x}>0.55$, representing Cu-0.5Ni alloy that contains 32 wt.% of Ni (Fig. 6a). Full reduction of the metals and formation of solid solution (Cu-0.5Ni alloy) is due to sufficient amount of the reducing agent (oil) and relatively high combustion temperatures ensuring the formation of reduced copper in the molten state that follows from the pictures shown in Fig. 7.

In the case of the $[Cu_2O-15wt.\%(oil)]-2NiO-\mathbf{x}(Nt)$ system complete reduction of the metals is observed within the interval $0.55<\mathbf{x}\leq0.9$ yielding a monophase Cu-Ni alloy that contains 48 wt.% of Ni at $\mathbf{x}=0.9$. At $\mathbf{x}>0.9$ due to an excess of the oxidizing agent, among the combustion products unreduced oxides remain too (Fig. 6b). Incompleteness of the reduction of metals is expressed also by the difference in the calculated (curve) and experimental (points) values of the mass loss (Fig. 5b).
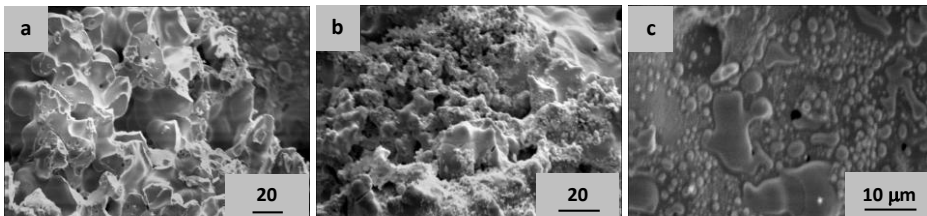

Fig. 7. Micrographs of fractures of the combustion product for the $[Cu_2O+15wt.\%(oil)]+NiO+0.75(Nt)$ mixture.

Thus, the results obtained demonstrated the possibility of complete reduction of both the metals and formation of Cu-0.5Ni and Cu-Ni composite powders or alloys under the combustion mode at using copper (I) oxide oily waste with 15 wt.% content of oil. Optimum conditions for obtaining Cu-0.5Ni and Cu-Ni alloys containing 32 and 48 wt.% Ni respectively were found out.

415

According to the selected optimum conditions, Cu-0.5Ni alloy was synthesized using copper oily waste with particle size less than 1.6 *mm*. The synthesis was carried out in the tubular SHS-3L reactor with the charge composition $[Cu_2O+15wt.\%\ (oil)]+NiO+0.75(Nt)$ and mass m=300 *g*.
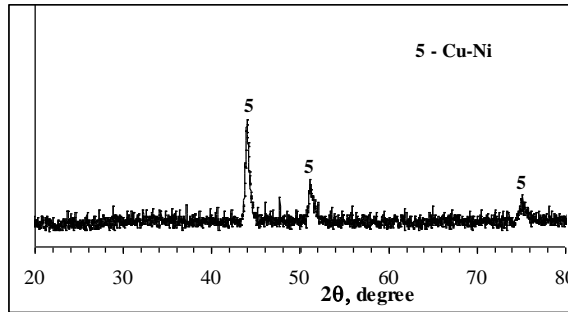

Fig. 8. XRD pattern of the final product synthesized in tubular SHS-3L reactor using 300 *g* of the initial $[Cu_2O+15wt.\%\ (oil)]+NiO+0.75(Nt)$ mixture.

Characterization of the obtained Cu-0.5Ni alloy was performed by XRD, SEM (Figs. 7, 8) and chemical analysis of free carbon. It should be noted, that at optimal conditions complete reduction of copper (I) oxide and nickel (II) oxide takes place with formation of a copper-nickel alloy and the combustion product represents a single-phase Cu-0.5Ni alloy with 0.15 wt.% of free carbon.

ԱՅՐՈՒՄԸ ՊՂՆՁԻ (I) ՕՔՍԻԴԱՅԻՆ ԹԱՓՈՆ-NiO-NH₄NO₃ ՀԱՄԱԿԱՐԳՈՒՄ ԵՎ Cu-Ni ՀԱՄԱՁՈՒԼՎԱԾՔՆԵՐԻ ՍԻՆԹԵԶԸ

Հ.Ա. ՄԱՀՄՈՒԴԻ, Վ.Վ. ՎԱՐԴԱՊԵՏՅԱՆ, Լ.Ս. ԱԲՈՎՅԱՆ և Ս.Լ. ԽԱՌԱՏՅԱՆ

Այրման պրոցեսում քիմիական ռեակցիաների ջերմային գումորդման մոտեցմամբ ուսումնասիրվել է պղնձի օքսիդային թափոնի և նիկելի (II) օքսիդի համատեղ վերականգնունմը՝ Cu+Ni կոմպոզիտային փոշիների և Cu-Ni համաձուլվածքի ստացման նպատակով: Այրման ալիքում երկու մետաղների վերականգնունմն իրականացվել է ամոնիումի նիտրատի (Nt) առկայության պայմաններում՝ առանց ներմուծելու որևէ այլ վերականգնիչ: Մետաղների ամբողջական վերականգնման համար ուսումնասիրվել են այրման օրինաչափությունները (Cu₂O թափոն-NiO-Nt) համակարգում՝ օգտագործելով հանքային յուղի տարբեր պարունակությամբ պղնձի օքսիդի (I) թափոններ և մետաղների օքսիդների տարբեր հարաբերակցությամբ ելային խառնուրդներ: Որոշվել են պղնձի օքսիդային թափոններից և NiO փոշուց Cu+Ni կոմպոզիտային փոշիների և Cu-Ni համաձուլվածքների ստացման օպտիմալ պայմանները՝ կախված յուղի և ամոնիումի նիտրատի պարունակությունից:

ГОРЕНИЕ В СИСТЕМЕ ОТХОДЫ ОКСИДА МЕДИ (I)-NiO-NH₄NO₃ И СИНТЕЗ СПЛАВОВ Cu-Ni

А. А. МАГМУДИ[1,3], В. В. ВАРДАПЕТЯН[1], Л. С. АБОВЯН[2] и С. Л. ХАРАТЯН[1,2]

[1]Ереванский государственный универсистет
Армения, 0025, Ереван, ул. А. Манукяна, 1
[2]Институт химической физики им. А.Б. Налбандяна НАН Республики Армения
Армения, 0014, Ереван, ул. П. Севака, 5/2
[3]Национальная иранская медная промышленная компания, Керман, Иран
E-mail: mahmoody.h@gmail.com
E-mail: larisa@ichph.sci.am

В работе применен метод термического сопряжения реакций для совместного восстановления меди и никеля из смеси отхода оксида меди и оксида никеля (II) в режиме горения с целью одностадийного получения композитных порошков Cu+Ni и сплавов Cu-Ni. Эксперименты по восстановлению металлов в волне горения осуществлялись в присутствии нитрата аммония (Nt) без введения какого-либо дополнительного восстановителя. Для достижения полноты восстановления были исследованы закономерности горения в системе (отходы Cu_2O-NiO-Nt) с использованием отходов оксида меди (I) с различным содержанием минерального масла и различным соотношением оксидов металлов в исходной смеси. Определены оптимальные условия получения композиционных порошков Cu+Ni и сплавов Cu-Ni из отходов оксида меди (I) и порошка NiO в зависимости от содержания масла и нитрата аммония.

REFERENCES

[1] *Handbook of Non-Ferrous Metal Powders.Technologies and Applications.* Oleg D. Neikov, Stanislav S., Naboychenko, Gordon Dowson, Eds., First edition, Amsterdam, Elsevier, 2009, Chapter 16.

[2] *Sharif Zein S.H., Mohamed A.R.* // IIUM Engineering Journal, 2004, v. 5, №1, p. 13.

[3] *Slade M.E.* An Econometric Model of the US Copper and Aluminum Industries: How Cost Changes Affect Substitution and Recycling, London: Routledge, 2018, Chapters 3–4.

[4] *Agrawal A., Kumari S., Sahu K.K.* // Ind. Eng. Chem. Res., 2009, v. 48, №13, p. 6145.

[5] *Sheih Sh.-W., Tsai, M.-Sh.* // Waste Manage. Res., 2000, v. 18, №5, p. 478.

[6] *Lebukhova N.V., Karpovich N.F.* // Inorg. Mater., 2008, v. 44, №8, p. 890.

[7] *L'vov, B.V.* // Thermochim.Acta, 2000, v. 360, №2, p. 109.

[8] *Merzhanov A.G.* // Ceramics International, 1995, v. 21, p. 371.

[9] *Merzhanov A.G.* // J. Mater. Chem., 2004, v. 14, p. 1779.

[10] *Yamukyan M.H., Manukyan Kh.V., Kharatyan S.L.* // Chem. Eng. J., 2008, v. 137, p. 636.

[11] *Kharatyan S.L.* / X Intern. Symposium on Self-propagating High-temperature Synthesis, 6-11 July, 2009, Tsakhkadzor, Armenia, Book of Abstracts, p. 62 (2009).

[12] *Kharatyan S.L.* "Metal powders". In "Concise Encyclopedia of Self-Propagating High-Temperature Synthesis". Ed. by *Inna P. Borovinskaya, Alexander A. Gromov, Evgeny A. Levashov, Yuri M. Maksimov, Alexander S. Mukasyan, Alexander S. Rogachev*, 2017, p.196.

[13] *Yamukyan M.H., Manukyan Kh.V., Kharatyan S.L.* // Chem. J. of Armenia, 2008 [in Russian], v. 61, №2, p. 159.

[14] *Kirakosyan H.V., Abovyan L.S., Kharatyan S.L.* // Chem. J. of Armenia, 2014 [in Russian], v. 67, №4, p. 363.

[15] *Abovyan L.S., Kharatyan A.S., Eliazyan D.S., Kharatyan S.L.* // Chem. J. of Armenia, 2017 [in Russian], v. 70, №3, p. 310.

[16] *Merzhanov A.G.* // Int. J. Self-Propag. High-Temp. Synth., 2011, v. 20, №1, p. 61.

[17] *Kharatyan S.L., Merzhanov A.G.* // Int. J. Self-Propag. High-Temp. Synth., 2012, v. 21, №1, p. 59.

[18] *Mahmoudi H.A., Abovyan L.S., Kharatyan S.L.* // Chem. J. of Armenia, 2017, v. 70, p. 477.

[19] *Mahmoudi H.A., Abovyan L.S., Aydinyan S.V., Kharatyan S.L.* // Int. J. Self-Propag. High-Temp. Synth., 2019, v. 28, №4, p. 233.